(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 558 113 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **93200312.2**

(22) Date of filing: **05.02.93**

(51) Int. Cl.5: **A23D 7/00**, A23L 1/19, A23L 1/24

(30) Priority: **26.02.92 EP 92301629**

(43) Date of publication of application:
01.09.93 Bulletin 93/35

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE

(71) Applicant: **UNILEVER N.V.**
P.O. Box 760
NL-3000 DK Rotterdam(NL)
(84) **GB IE**

(71) Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)
(84) **BE CH DE DK ES FR GR IT LI NL PT SE AT**

(72) Inventor: **Campbell, Iain James**
Unilever Research Colworth Lab., Colworth House
Sharnbrook, Bedford MK44 1LQ(GB)
Inventor: **Morley, Wayne Gerald**
Unilever Research Colworth Lab., Colworth House
Sharnbrook, Bedford MK44 1LQ(GB)
Inventor: **Norton, Ian Timothy**
Unilever Research Colworth Lab., Colworth House
Sharnbrook, Bedford MK44 1LQ(GB)

(74) Representative: **Hartong, Richard Leroy et al**
Unilever N.V. Patent Division P.O. Box 137
NL-3130 AC Vlaardingen (NL)

(54) Water-continuous emulsions based on polysaccharides.

(57) The invention concerns water-continuous emulsions having a fat content of 1-60 wt.%, and wherein the aqueous phase consists of a gelling polysaccharide capable of forming a gel while the shear modulus of the aqueous phase must fulfil specific requirements and while the gelling polysaccharides are present as microgels with a mean equivalent diameter of less than 100 μm.

The emulsion is spoonable, meaning that it fulfils specific requirements as to yield value, Bingham viscosity and failure to stress.

The emulsions can be used in non-dairy creams, in dressings and mayonnaises.

EP 0 558 113 A1

Liquid-based compositions comprising at least one gelling polysaccharide capable of forming a gel, wherein the composition, at temperature T, is fluid and the shear modulus of the composition, at temperature T, is three or more times lower than the shear modulus of the gel obtained either after heating said composition to above the transition temperature and subsequent cooling or after chemically setting of the gelling agent, under quiescent conditions at the same temperature T. The gelling polysaccharide(s) predominantly being present in the composition as microgels having a mean equivalent diameter of less than 100 μm, more preferably of less than 50 μm. Microgels of this type are known from our European patent applications 355,908 and 432,835

Furthermore, it is disclosed that these compositions are pourable and pumpable and that they disrupt at low strain. A method for the preparation of these compositions is also disclosed in these documents.

It is further disclosed that these compositions can be applied in edible, water-continuous fat emulsions. However, application of these compositions in food products that are spoonable, is not disclosed in these earlier Unilever patent applications.

We have now found that these compositions are very helpful in the preparation of water-continuous fat emulsions with the desired rheology in order to make them eminently spoonable.

Spoonable emulsions are defined in our earlier European patent applications 91310097.0 and 91310098.8. A spoonable emulsion is defined by its rheological behaviour, i.e. an emulsion displaying, at 5 °C, the following rheology :

- a yield value of > 50 Pa, when extrapolating from shear rates between 100 and 300 S^{-1};
- Bingham viscosities < 500 mPa.s between shear rates of 100 and 300 S-1;
- failure to stress at a strain of < 0.5 Radians.

Therefore, our invention concerns water-continuous emulsions, wherein the above-mentioned liquid-based compositions comprising a gelling polysaccharide are present and which display excellent spoonable characteristics.

Thus, our invention is concerned with a water-continuous emulsion, which optionally contains protein component(s), emulsifier(s) and/or thickener(s), wherein the fat phase comprises 1-60 wt.% of the total composition and the aqueous phase consists of at least one gelling polysaccharide capable of forming a gel, wherein the aqueous phase, at temperature T, is fluid and wherein the aqueous phase, at temperature T, has a shear modulus that is at least three times as low as the shear modulus of the gel obtained, under quiescent conditions at the same temperature T, while the gelling polysaccharides are present as microgels with a mean equivalent diameter of less than 100 μm and the emulsion is spoonable, according to our definition for spoonable.

The water phase can be obtained either by shearing of the polysaccharides, using a specific heating regime or by chemically setting of the polysaccharides under shear.

Therefore, our invention is concerned with water-continuous fat emulsions wherein the aqueous phase consists of at least one gelling polysaccharide capable of forming a reversible gel and wherein the aqueous phase, at temperature T, has a shear modulus that is at least three times as low as the shear modulus of the gel obtained after heating said composition to above the transition temperature and subsequent cooling under quiescent conditions to the same temperature T.

Further, our invention concerns fat emulsions wherein the aqueous phase consists of at least one chemically set gelling polysaccharide capable of forming a gel and wherein the aqueous phase, at temperature T, has a shear modulus that is at least three times as low as the shear modulus obtained under quiescent conditions.

Definitions for transition temperature, gel melting point, mean equivalent diameter, shear modulus, gel setting point, and methods for measuring these parameters can be found in our earlier European patent application 355,908. These definitions and methods should be considered to be incorporated into this application. Methods and compounds for the preparation of chemically set polysaccharides can be found in European patent application 432,835.

Definitions for yield value, Bingham viscosity and failure to stress and methods for measuring them can be found in P.Sherman, Emulsion Science, Academic press, 1968, and in our European patent applications 91310097.0 and 91310098.8.

Our new emulsions can be applied in non-dairy creams, dressings and mayonnaises.

The fat phase of our new emulsions represents in general 1-60 wt.% of the total emulsion. In non-dairy creams, a fat content of 2-40 wt.% is preferred; however, a fat content of 3-20 wt.% is most preferred, while in dressings and mayonnaises a fat content of 2-45 wt.% is preferred and 3-35 wt.% is most preferred. This means therefore that we have now found new food products that can have very low fat contents while their characteristics, such as mouthfeel, whipping time, rheology, firmness and overrun, are excellent. Thus, we have found products that are healthier (because of the very low fat content) than known products, while their

physical and organoleptic properties are about the same as the properties of known products. For example, whipping times of less than 6 minutes (using a Kenwood Electronic mixer model Km.201, 500 Watt, applying 180 rpm and a wire-whisk) are easily achievable.

The amount of gelling polysaccharide in the water phase can be 0.1-15 wt.%. The preferred amounts depend on the type of polysaccharide. For agar the preferred range is 0.2-5 wt.%; for carrageenan and furcellaran the preferred range is 0.5-10 wt.%.

The sheared polysaccharides that are suitably applied in the water phase of our emulsions can be chosen from the group consisting of agar, kappa-carrageenan, iota-carrageenan, pectin, alginate, gellan, furcellaran or mixtures thereof.

In order to impart a dairy character (i.e. dairy-like taste) to the emulsions, if required, incorporation of 2-10 wt.% of a protein component is preferred, in particular buttermilk powder or skimmed milk powder.

Although not always necessary, it is often advantageous to incorporate an emulsifer system into our emulsions. In this way, the whipping and spoonable properties of our products can be influenced. In principle, any known type of emulsifier can be used. Preferred emulsifiers, however, are monoglycerides of saturated and/or unsaturated fatty acids (in particular C_{16}-C_{18} acids); polyoxyethylene sorbitan fatty acid esters; diacetyl tartaric esters of mono- or diglycerides (or the analogues without acetyl groups); lecithins; lactic acid esters of mono- and/or diglycerides or combinations thereof. The amount of emulsifier is usually 0.05-1.5 wt.%, in particular 0.1-0.8 wt.%.

It is also possible to control the rheology of our emulsions to some extent by adding a thickener to the cream phase of our products. Suitable thickeners can be chosen from the group consisting of locust bean gum, xanthan gum, guar gum, sodium alginate, pectin or carrageenan or mixtures thereof. Note that these components of the cream phase are not sheared and are therefore different from the other components present in the water phase. Amounts of 0.05-1.5 wt.% of thickener, based on the product, lead to very acceptable results.

The emulsions according to the invention can be prepared by the following process :

1) a fluid composition containing at least one gelling polysaccharide is made by adding the polysaccharide to water, at a temperature above 60 °C, subjecting this mixture to sufficient shear while cooling the liquid slowly through its gel setting temperature and collecting the composition, which displays a less rigid structure than the quiescently gelled composition;

2) a water-continuous fat emulsion is made, containing fat, protein, emulsifier and thickener;

3) the emulsion of 2) is homogenized under pressure (50-200 bar, single stage, preferably);

4) the compositions of 1) and 3) are mixed in a predetermined ratio.

Alternatively, the fluid composition of 1) may be kept at a temperature above 60 °C and mixed with the emulsion of 3) before cooling and shearing.

Similar processes can be performed by using a chemically set gelling agent (e.g. by Ca^{2+}-ions). In that case, the gelling polysaccharide is chemically set by addition of a chemically setting compound while shearing the fluid composition.

For the preparation of dressings or mayonnaises the above-mentioned processes are adapted in such a way that new dressings and mayonnaises are produced.

EXAMPLES

Spoonable creams were prepared by mixing an agar phase and a cream phase. The agar phase was made as follows :

Agar (Gracilona® 125)	5%
Water	95%

1. The agar was dissolved in the water at 90 °C to give a 5 wt.% agar solution.
2. The solution was pumped through a micro-votator spreads line, in which the following conditions were applied :

Unit	Speed (rpm.)	Exit T °C
A_1	4,000	18.2
C_1	4,000	10.5
A_2	1,400	23.1
A_3	1,400	8.9

The throughput was 56 g/min.

The cream phase was made up as follows :

Hardened palmkernel oil	24%
Coconut oil	24%
BMP (butter milk powder)	7%
Emulsifier	0.6%
Thickener	0.05%
Water	44.35%

1. BMP, emulsifier and thickener were dissolved in the water at 80 °C.
2. The fat blend was mixed into the aqueous phase with the aid of a Silverson mixer.
3. The product of 2) was homogenized (single stage, 100 bar) and then rapidly cooled to 5 °C.

This resulted in a 48% fat oil-in-water (o/w) emulsion.

Spoonable creams were made by carefully mixing a sample of the sheared 5% agar dispersion with a sample of the 48% fat o/w emulsion. Each resulting dispersion was stored overnight at 5 °C. The rheological and whipping properties were as follows :

Example 1

Formulation - 188.1 g of sheared 5% agar dispersion 13.0 g of 48% fat o/w emulsion
Overall - 4.7% agar and 3.1% fat on product

Extrapolated yield stress	238 Pa
Bingham viscosity	261 mPas
Failure to stress	0.021 Radians

Example 2

Formulation - 161.8 g of sheared 5% agar dispersion 38.3 g of 48% fat o/w emulsion
Overall - 4.0% agar and 9.2% fat on product

Extrapolated yield stress	144 Pa
Bingham viscosity	251 mPas
Failure to stress	0.014 Radians

179 g were whipped on a Kenwood Chef at 180 rpm.

Whipping time	4 min. 30 sec.
Overrun	73%
Firmness (Boucher)	81

Example 3

Formulation - 126.2 g of sheared 5% agar dispersion 73.2 g of 48% fat o/w emulsion
Overall - 3.2% agar and 17.6% fat on product

Extrapolated yield stress	70 Pa
Bingham viscosity	176 mPas
Failure to stress	0.034 Radians

174 g were whipped on a Kenwood Chef at 180 rpm.

Whipping time	3 min. 47 sec.
Overrun	127%
Firmness (Boucher)	80

Example 4

A 5% oil mayonnaise was prepared, using the sheared 5% agar dispersion, according to the following recipe:

Recipe	
4.7 wt%	agar
5.0 wt%	sunflower oil
0.13 wt%	K-sorbate
1.5 wt%	NaCl
0.002 wt%	dill aroma
0.0005 wt%	lemon aroma
1.2 wt%	mustard
	acetic acid to pH = 3.7
trace β-carotene for colour	
87.4 wt%	water

The aqueous agar-phase and the other components were mixed with a high speed mixer.

Results	
Extrapolated yield stress	256 Pa
Bingham viscosity	479 mPa.s
Failure to stress	0.024 Radians

Example 5

In a way similar to example 4 a mayonnaise was made, containing 30 wt% oil.

Recipe	
3.5 wt%	agar
30.0 wt%	sunflower oil
0.13 wt%	K-sorbate
1.5 wt%	NaCl
0.002 wt%	dill aroma
0.0005 wt%	lemon aroma
1.2 wt%	mustard
	acetic acid to pH = 3.7
trace β-carotene	
63.7 wt%	water

Results	
Extrapolated yield stress	161 Pa
Bingham viscosity	241 mPa.s
Failure to stress	0.048 Radians

Example 6

In a way similar to example 4 a dressing was made. The aqueous agar-phase was the same as applied in example 4.

Recipe	
2.0 wt%	agar
0.13 wt%	K-sorbate
1.1 wt%	NaCl
7.8 wt%	mixed flavours (garlic; onion; mustard; black pepper)
88.97	water
	pH adjusted to 4.0 with acetic acid

Results	
Extrapolated yield stress	106 Pa
Bingham viscosity	161 mPa.s
Failure to stress	0.027 Radians

Claims

1. A water-continuous emulsion, which optionally contains protein component(s), emulsifier(s) and/or thickener(s), wherein the fat phase comprises 1-60 wt.% of the total composition and the aqueous phase consists of at least one gelling polysaccharide capable of forming a gel, wherein the aqueous phase, at temperature T, is fluid and wherein the aqueous phase, at temperature T, has a shear modulus that is at least three times as low as the shear modulus of the gel obtained under quiescent conditions at the same temperature T, while the gelling polysaccharides are present as microgels with

a mean equivalent diameter of less than 100 µm, and the emulsion is spoonable.

2. Water-continuous emulsion according to Claim 1, wherein the aqueous phase consists of at least one gelling polysaccharide capable of forming a reversible gel and wherein the aqueous phase, at temperature T, has a shear modulus that is at least three times as low as the shear modulus of the gel obtained after heating said composition to above the transition temperature and subsequent cooling under quiescent conditions to the same temperature T.

3. Water-continuous emulsion according to Claim 1, wherein the aqueous phase consists of at least one chemically set gelling polysaccharide capable of forming a gel and wherein the aqueous phase, at temperature T, has a shear modulus that is at least three times as low as the shear modulus obtained under quiescent conditions.

4. Water-continuous emulsion according to Claim 1, wherein the emulsion shows the following rheological behaviour at 5 °C :
   - it has a yield value of > 50 Pa, when extrapolating from shear rates between 100 and 300 S^{-1};
   - it has a Bingham viscosity < 500 mPa.s between shear rates of 100 and 300 S-1;
   - it shows failure to stress at a strain of < 0.5 Radians.

5. Water-continuous emulsion according to Claim 4, wherein the emulsion displays simultaneously a whipping time of less than 6 minutes (using a Kenwood whipping apparatus).

6. Water-continuous emulsion according to Claims 1-5, wherein the emulsion is a non-dairy cream with a fat content of 2-40 wt.%.

7. Water-continuous emulsion according to Claims 1-5, wherein the emulsion is incorporated in a dressing or a mayonnaise and has a fat content of 2-45 wt.%.

8. Water-continuous emulsion according to Claim 1, wherein the polysaccharide concentration of the water phase is 0.1-15 wt.%.

9. Water-continuous emulsion according to Claims 1-8, wherein the polysaccharide is chosen from the group consisting of agar, kappa-carrageenan, iota-carrageenan, gellan, furcellaran, pectin, alginate and mixtures thereof.

10. Water-continuous emulsion according to Claim 6, wherein the composition contains 2-10 wt.% of a protein, preferably butter milk powder or skimmed milk powder.

11. Water-continuous emulsion according to Claim 1, wherein the emulsifier is chosen from the group consisting of monoglycerides of saturated and/or unsaturated fatty acids (in particular C_{16}-C_{18} acids); polyoxyethylene sorbitan fatty acid esters; diacetyl tartaric esters of mono- or diglycerides (or the analogues without acetyl groups); lecithins; lactic acid esters of mono- and/or diglycerides or combinations thereof, and is present in an amount of 0.05-1.5 wt.%.

12. Water-continuous emulsion according to Claim 1, wherein the thickener is present in an amount of 0.05-1.5 wt.% and is chosen from the group consisting of locust bean gum, xanthan gum, guar gum, sodium alginate, pectin, carrageenan or mixtures thereof.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 20 0312
Page 1

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 291 228 (MERCK & CO.INC.) * column 8, line 9 - line 10; claims 1-7; figure 3 *	1-4	A23D7/00 A23L1/19 A23L1/24
A		7-9	

D,Y	EP-A-0 355 908 (UNILEVER NV) * claims 1-9; example 14 *	1,2,4	

D,Y	EP-A-0 432 835 (UNILEVER NV) * claims 1-14 *	1,3,4	

E	EP-A-0 483 896 (UNILEVER NV) * claims 1-14 *	1,4	

A	EP-A-0 455 288 (UNILEVER NV) * claim 1 *	1,4,5	

A	EP-A-0 463 688 (UNILEVER NV) * page 1, line 3 - line 5 * * page 3, line 43 - line 48; claims 1,5,7,8,10-12 *	1-4,7-12	
	---		TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	DATABASE WPIL Week 9206, Derwent Publications Ltd., London, GB; AN 92-046794 & SU-A-1 648 321 (FOOD IND CORRSP INS) 15 May 1991 * abstract *	1,7-9	A23D A23L

A	EP-A-0 005 030 (MERCK & CO.INC.) * page 11, line 12 - line 19; examples 9,10 *	1	

A	EP-A-0 441 495 (PFIZER INC.) * page 6, line 52 - page 7, line 17 * * page 8, line 25 - line 27; claims 1-14 *	1	

	-/--		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28 MAY 1993	DEKEIREL M.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 20 0312

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DD-A-152 582 (AKADEMIE DER WISSENSCHAFTEN DER DDR) * page 2, paragraph 4 * * page 4, paragraph 5 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28 MAY 1993	DEKEIREL M.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0601)